THE STRANGE HISTORY OF B FUNCTIONS OR HOW THEORETICAL CHEMISTS AND MATHEMATICIANS DO (NOT) INTERACT

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Abstract

B functions are a class of relatively complicated exponentially decaying basis functions. Since the molecular multicenter integrals of the much simpler Slater-type functions are notoriously difficult, it is not at all obvious why B functions should offer any advantages. However, B functions have Fourier transforms of exceptional simplicity, which greatly simplifies many of their molecular multicenter integrals. This article discusses the historical development of B functions from the perspective of the interaction between mathematics and theoretical chemistry, which traditionally has not been very good. Nevertheless, future progress in theoretical chemistry depends very much on a fertile interaction with neighboring disciplines.

Contents

1 Introduction

Molecular electronic structure theory tries to explain the nature of molecules and their properties by doing calculations on the basis of quantum mechanics. This approach is obviously possible, but as we all know, numerous obstacles have to be overcome. Already in 1929, Dirac had stated [1, p. 714]:

> The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

It is noteworthy that Dirac only mentioned atomic calculations. Apparently it was at that time more or less unthinkable to do meaningful molecular calculations. But since the time of Dirac, there has been enormous progress in particular in numerical and applied mathematics. Moreover, we have witnessed a computer revolution which now gives us a computing power that was beyond imagination in 1929. Accordingly, we now have much better chances of accomplishing our aims. Chemical insight via quantum mechanical calculations is no longer utopia.

Nevertheless, the central methodological problem addressed by Dirac – the development of powerful approximation techniques – has not really changed. The reduction of chemical phenomena to *manageable* computational problems has been and still is far from trivial. In spite of the theoretical and technological advances of recent years, the computational complexity of sufficiently accurate quantum mechanical calculations is still prohibitive, and molecular electronic structure calculations are only feasible if we make some partly very drastic approximations.

Thus, progress depends quite crucially on our ability of reformulating and translating chemical intuition to a mathematical formalism, which does better than the currently available approximation procedures and which ultimately helps to make more accurate calculations on larger molecules possible.

Optimists might argue that future advances in computer hard- and software will be enough to achieve this goal. However, I am not so optimistic. In the long run, we will also need substantial progress in mathematics. But this will to a large extend depend on a fruitful collaboration between theoretical chemists interested in methodological questions and mathematicians interested in scientific applications.

In theoretical chemistry, there is the widespread believe that the parentage of atoms facilitates our attempts of understanding the electronic structure of molecules. Thus, in molecular calculations on the basis of the Hartree-Fock-Roothaan equations [2, 3, 4], effective one-particle wave functions (MOs) are usually approximated by a linear combination of so-called *basis functions* or *atomic orbitals* (AOs) centered at the Ω different nuclei of the molecule:

$$\psi(\boldsymbol{r}) \;=\; \sum_{\alpha=1}^{\Omega} \sum_{n=1}^{N} C_n^{\alpha}\, \varphi_n(\boldsymbol{r} - \boldsymbol{R}_\alpha)\,. \qquad (1.1)$$

The fundamental entities in this LCAO-MO approach are the basis functions $\{\varphi_n(\boldsymbol{r})\}_{n=1}^{N}$. Basis functions and their derivatives up to a certain order must be square integrable with respect to an integration over the whole $\mathbb{R}^3$, and they also have to be complete in the corresponding Hilbert and Sobolev spaces, but otherwise they are essentially arbitrary.

There are, however, two additional requirements of utmost practical relevance which *good* basis functions should satisfy:

1. Already short linear combinations of the type of (1.1) should provide sufficiently accurate approximations, i.e., the summation limit N in (1.1) should be as small as possible.

2. The molecular multicenter integrals, which occur inevitably in the LCAO-MO approach, should possess a manageable complexity.

It is not too difficult to satisfy the first requirement by taking into account what we know about the exact solutions of effective one-particle atomic and molecular Schrödinger equations. Kato [5] had shown that the singularities of the potential of atomic and molecular Hamiltonians produce discontinuities of the wave functions commonly called Coulomb or correlation cusps. Moreover, exact solutions of these Hamiltonians decay *exponentially* at large distances (see for example [6, 7] and references therein).

These properties of exact solutions clearly favor Slater-type functions [8, 9], which were originally introduced to provide computationally convenient approximations to numerically determined solutions of

effective one-particle equations. In unnormalized form, they can be expressed as follows:

$$\chi_{N,L}^M(\beta, \mathbf{r}) \;=\; (\beta r)^{N-L-1}\, \mathrm{e}^{-\beta r}\, \mathcal{Y}_L^M(\beta \mathbf{r})\,. \quad (1.2)$$

Here, $\mathbf{r} \in \mathbb{R}^3$, $\mathcal{Y}_L^M(\beta \mathbf{r}) = (\beta r)^L Y_L^M(\theta, \phi)$ is a regular solid harmonic and $Y_L^M(\theta, \phi)$ is a (surface) spherical harmonic, $\beta > 0$ is a scaling parameter, N is a generalized principal quantum number which is in most cases, but not always a positive integer $\geq L+1$, and L and M are the usual (orbital) angular momentum quantum numbers.

Slater-type functions were used with considerable success in atomic calculation, and there is no reasonable doubt that their use in molecular calculations would also be highly desirable. Unfortunately, Slater-type functions are not able to satisfy the second requirement mentioned above: The evaluation of their molecular multicenter integrals turned out to be extremely difficult, and in spite of the heroic efforts of numerous researchers, no completely satisfactory solution has been found yet. Actually, the efficient and reliable evaluation of multicenter integrals of Slater-type functions is among the oldest mathematical and computational problems of molecular electronic structure theory. A review of the older literature can be found in an article by Dalgarno [10]. Another useful review is the one by Harris and Michels [11].

Because of the problems with the efficient and reliable evaluation of the notorious multicenter integrals of Slater-type functions, molecular electronic structure calculations are now dominated by Gaussian basis functions which have many disadvantages: They are unphysical because they cannot reproduce a Coulomb cusp, and for large distances they also decay much faster than exponentially. Accordingly, fairly large values of N in (1.1) are needed to produce sufficiently accurate results. In fact, Gaussian basis functions have only one, albeit decisive advantage: Their molecular multicenter integrals can be computed comparatively easily.

In spite of the clear dominance of Gaussian functions, the search for alternative basis functions, that are more physical than Gaussians and whose multicenter integrals can be computed more easily than the notoriously difficult multicenter integrals of Slater-type functions, has been continued by numerous researchers. In this article, I want to discuss the history and most interesting features of a class of exponentially decaying basis functions, the so-called B functions, that were – based on previous work by

Shavitt [12, Eq. (55) on p. 15] – defined by Filter and Steinborn [13, Eq. (2.14)] as follows:

$$B_{n,\ell}^m(\beta, \mathbf{r}) \;=\; \frac{\hat{k}_{n-1/2}(\beta r)\, \mathcal{Y}_\ell^m(\beta \mathbf{r})}{2^{n+\ell}(n+\ell)!}\,. \quad (1.3)$$

Here, $\beta > 0$, $n \in \mathbb{Z}$, and $\hat{k}_{n-1/2}$ is a reduced Bessel function. If $K_\nu(z)$ is a modified Bessel function of the second kind [14, p. 66], the reduced Bessel function with in general complex ν and z is defined as follows [15, Eqs. (3.1) and (3.2)]

$$\hat{k}_\nu(z) \;=\; (2/\pi)^{1/2}\, z^\nu\, K_\nu(z)\,. \quad (1.4)$$

If the order ν is half-integral, $\nu = n + 1/2$ with $n \in \mathbb{N}_0$, a substantial simplification takes place: Then, the reduced Bessel function is an exponential multiplied by a terminating confluent hypergeometric series $_1F_1$ (see for example [16, Eq. (3.7)]):

$$\begin{aligned}\hat{k}_{n+1/2}&(z)\\ &= \; 2^n\,(1/2)_n\, \mathrm{e}^{-z}\,_1F_1(-n; -2n; 2z)\,. \quad (1.5)\end{aligned}$$

Obviously, B functions are fairly complicated mathematical objects. Moreover, (1.3) and (1.5) imply that B functions can be expressed as a linear combination of Slater-type functions defined by (1.2). Hence, it is not at all clear why the use of the comparatively complicated B functions should offer any advantages over Slater-type functions which possess an exceptionally simple explicit expression.

If we form finite linear combinations of Slater-type functions and do some mathematical manipulations, then the complexity of the resulting expression normally increases, depending on the number of Slater-type functions occurring in the linear combination. In fortunate cases, however, it may happen that most terms of the resulting expression cancel exactly. Thus, a significant reduction of complexity by forming linear combinations is also possible.

The topic of this article are B functions and their role in the theory of multicenter integrals. However, research on multicenter integrals is essentially mathematical in nature. Quantum mechanics only determines which integrals we evaluate, but the techniques employed for their evaluations are entirely mathematical. Physical insight is of secondary importance. What really matters are mathematical skills.

Thus, a discussion of B functions immediately raises another, very profound question about the role of mathematics in molecular electronic structure theory, and how well and how rapidly new advances in mathematics are incorporated into electronic structure theory.

Essentially this boils down to the question whether and how well theoretical chemists interested in methodological questions and mathematicians are interacting and – in the best of all worlds – even collaborating. As I had argued in [17, Section 1], science is now highly fragmented and consists of almost completely disjoint subfields. As a consequences of this probably unavoidable specialization, communication between researchers belonging to different subfields has deteriorated quite a bit and no longer functions as well as it should.

Molecular electronic structure theory is a highly interdisciplinary research topic whose progress depends crucially on a functioning communication with and input from neighboring disciplines. Ultimately, computational chemistry has become feasible because of the spectacular advances in computer hard- and software. However, mathematics is the basis of all computing and not all problems can be solved by using more powerful computers. One should also not forget that Pople, whose suite of Gaussian programs has contributed greatly to the computerization of chemistry, had done his undergraduate studies in mathematics, and later he had been reader in mathematics at the University of Cambridge.

It is my central hypothesis that it should be in the self-interest of theoretical chemists to improve communication with mathematicians. Traditionally, this communication has been fairly bad. In my opinion, the history of B functions provides ample evidence supporting this claim.

2 Bessel Polynomials

Polynomials associated with the names of Legendre, Gegenbauer, Jacobi, Hermite, and Laguerre certainly belong to the pillars of classical analysis, and they are also of considerable importance in quantum theory and other scientific disciplines.

There are several other, less important classes of polynomials with well established properties. Many of these polynomials are completely ignored by theoretical physicists or chemists, because they have no obvious physical relevance. Such a pragmatic attitude is certainly justified. Nevertheless, occasional surprises cannot be ruled out.

For example, in the later stages of my PhD thesis [18] I became aware of a book by Grosswald [19] from which I learned that the polynomial part in (1.5) and thus also reduced Bessel functions had already been treated in the mathematical literature. For the poly-

nomial part of reduced Bessel functions, the notation

$$\theta_n(z) = \mathrm{e}^z \, \hat{k}_{n+1/2}(z) \qquad (2.1)$$

is used in the mathematical literature [19, Eq. (1) on p. 34]. Together with some other, closely related polynomials, the $\theta_n(z)$ are called *Bessel polynomials* [19]. According to Grosswald [19, Section 14], they have been applied in such diverse and seemingly unrelated fields as number theory, statistics, and the analysis of complex electrical networks.

The Bessel polynomials $\theta_n(z)$ occur also in a completely different mathematical context which later became very important for me. In the book by Baker and Graves-Morris [20, p. 8] on Padé approximants, it is remarked that Padé had shown in his seminal thesis [21] that the Padé approximant $[n/m]$ with $n, m \in \mathbb{N}_0$ to the exponential function $\exp(z)$ can be expressed as the ratio of two terminating confluent hypergeometric series [20, Eq. (2.12)]:

$$[n/m] = \frac{{}_1F_1(-n; -n-m; z)}{{}_1F_1(-m; -n-m; -z)} . \qquad (2.2)$$

Accordingly, the diagonal Padé approximant with $n = m$ to the exponential function can be expressed as the ratio of two Bessel polynomials:

$$[n/n] = \frac{\theta_n(z/2)}{\theta_n(-z/2)} , \qquad n \in \mathbb{N}_0 . \qquad (2.3)$$

3 Shavitt's Gauss Integral Representation

We can safely assume that Bessel polynomials were completely unknown among theoretical chemists. Thus, the usefulness of reduced Bessel functions had to be discovered differently.

It seems that Shavitt was the first theoretical chemist who noticed that reduced Bessel functions have in spite of their undeniable complexity some very useful features. In tables of Laplace transforms, one can find the following relationship (see for example [22, Eq. (13.42) on p. 338]):

$$s^{\nu/2} \, K_\nu\big(as^{1/2}\big) = a^\nu \int_0^\infty \frac{\mathrm{e}^{-st-a^2/(4t)}}{(2t)^{\nu+1}} \, \mathrm{d}t . \qquad (3.1)$$

Setting $s = z^2$ and $a = 1$ yields the following remarkably simple Gaussian integral representation of the reduced Bessel function [12, Eq. (55) on p. 15]:

$$\hat{k}_\nu(z) = (2/\pi)^{1/2} \int_0^\infty \frac{\mathrm{e}^{-z^2t-1/(4t)}}{(2t)^{\nu+1}} \, \mathrm{d}t . \qquad (3.2)$$

Shavitt defined the reduced Bessel function according to $k_\lambda(z) = z^\lambda K_\lambda(z)$. Unfortunately, this notation is misleading because $k_\lambda(z)$ can easily be confounded with the *spherical* modified Bessel function $k_n(z) = [\pi/(2z)]^{1/2} K_{n+1/2}(z)$ with $n \in \mathbb{N}_0$. Therefore, Steinborn and Filter [15, Eqs. (3.1) and (3.2)] defined reduced Bessel functions via (1.4). The introduction of the prefactor $(2/\pi)^{1/2}$ in (1.4) has the additional advantage that it simplifies most formulas.

A Gauss integral representation for Slater-type functions can also be constructed. The starting point would be the following following Laplace transform (see for example [22, Eq. (5.94) on p. 259]):

$$s^\nu \exp\left(-as^{1/2}\right) = [2/\pi]^{1/2}$$
$$\times \int_0^\infty \frac{\mathrm{e}^{-st-a^2/(8t)}}{(2t)^{\nu+1}} D_{2\nu+1}\left(a/[2t]^{1/2}\right) \mathrm{d}t. \quad (3.3)$$

Here, $D_{2\nu+1}\left(a/[2t]^{1/2}\right)$ is a parabolic cylinder function [14, p. 324] which is a special case of the Whittaker function $W_{\kappa,\mu}(z)$ of the second kind [14, p. 296]. Accordingly, the Laplace transform (3.3) is much more complicated than (3.1). Obviously, this conclusion applies also to the Gauss transform for Slater-type functions that can be derived from (3.3).

The remarkably compact Gauss integral representation (3.2) inspired Shavitt [12, p. 16] to propose the use of reduced Bessel functions as alternative exponentially decaying basis functions in electronic structure calculations. This was done in articles by Bishop and Somorjai [23], Somorjai and Yue [24], and Yue and Somorjai [25].

The Gaussian function in (3.2) makes it possible to reduce multicenter integrals involving reduced Bessel functions to the corresponding integrals of Gaussians, which can be evaluated comparatively easily, multiplied by integrals over *nonphysical* variables. Unfortunately, the remaining integrations can normally only be done numerically. Therefore, this approach is apparently not efficient enough to provide a viable approach for the evaluation of multicenter integrals of reduced Bessel functions.

4 The Gegenbauer Addition Theorem of Reduced Bessel Functions

Multicenter integrals are difficult to evaluate because the integration variables are not separated. Principal tools, which can accomplish such a separation of variables, are so-called *addition theorems*. These are expansions of a given function $f(\boldsymbol{r} \pm \boldsymbol{r}')$ with $\boldsymbol{r}, \boldsymbol{r}' \in \mathbb{R}^3$ in terms of other functions that only depend on either $\boldsymbol{r}$ or $\boldsymbol{r}'$. The best known example of such an addition theorem is the Laplace expansion of the Coulomb potential in terms of spherical harmonics, which is nothing but the well known generating function $\left[1 - 2xz + z^2\right]^{-1/2}$ of the Legendre polynomials [14, p. 232] is disguise.

The modified Bessel function $w^{-\nu} K_\nu(\gamma w)$ with $w = \left[\rho^2 + r^2 - 2r\rho\cos\theta\right]^{1/2}$, $0 < \rho < r$, and $\nu \in \mathbb{C} \setminus \mathbb{N}_0$ possesses the following Gegenbauer-type addition theorem [14, pp. 106 - 107]:

$$w^{-\nu} K_\nu(\gamma w) = 2^\nu \gamma^{-\nu} \Gamma(\nu) (r\rho)^{-\nu}$$
$$\times \sum_{n=0}^\infty C_n^\nu(\cos\theta) I_{\nu+n}(\gamma\rho) K_{\nu+n}(\gamma r). \quad (4.1)$$

Here, $C_n^\nu(\cos\theta)$ is a Gegenbauer polynomial [14, p. 218], and $I_{\nu+n}(\gamma\rho)$ is a modified Bessel function of the first kind [14, p. 66].

Comparison with (1.4) shows that the addition theorem (4.1) is essentially a Gegenbauer-type addition theorem of the reduced Bessel function $\hat{k}_{-\nu}(\gamma w)$. A very important special case occurs for $\nu = 1/2$ because then the Gegenbauer polynomial becomes a Legendre polynomial according to $C_n^{1/2}(x) = P_n(x)$ [14, p. 219], yielding the Legendre-type addition theorem of the Yukawa potential [14, p. 218]:

$$\frac{\mathrm{e}^{-\gamma w}}{w} = (r\rho)^{-1/2} \sum_{n=0}^\infty (2n+1) P_n(\cos\theta)$$
$$\times I_{n+1/2}(\gamma\rho) K_{n+1/2}(\gamma r). \quad (4.2)$$

With the help of the so-called addition theorem of the Legendre polynomials [26, p. 303]

$$P_\ell(\cos\theta) = \frac{4\pi}{2\ell + 1}$$
$$\times \sum_{m=-\ell}^\ell \left[Y_\ell^m(\boldsymbol{r}/r)\right]^* Y_\ell^m(\boldsymbol{r}'/r'), \quad (4.3)$$

where $\cos\theta = \boldsymbol{r}\boldsymbol{r}'/(rr')$, the Legendre-type addition theorem (4.2) can be converted to an expansion in terms of spherical harmonics.

This addition theorem for the Yukawa potential was the starting point for the so-called zeta function method of Barnett and Coulson [27]. They tried to construct an addition theorem for Slater-type functions by applying suitable *generating differential operators* to this addition theorem. Unfortunately, this idea did not lead to a complete success in the case

of Slater-type functions. Due to technical problems it was not possible to perform all differentiations in closed form. Consequently, the coefficients of the zeta function expansion could only be computed recursively, but not in explicit form [27, 28].

Later, numerous other researchers worked on addition theorems for Slater-type functions (see for example [29, Refs. 33 - 50, 52, 65, 84, 85, 90, 91]). But all these addition theorems turned out to be fairly complicated. I suspect that there is still plenty of room for improvements.

The technical problems with the zeta function method of Barnett and Coulson [27] in special and with addition theorems for Slater-type functions in general inspired Steinborn and Filter to derive an addition theorem for reduced Bessel functions directly from the Gegenbauer expansion (4.1). This was much easier than the derivation of analogous addition theorems for scalar Slater-type functions.

Let us assume that a Gegenbauer-type addition of the type of (4.1) for some function is known. If the Gegenbauer polynomials in this expansion can be replaced by a finite sum of Legendre polynomials, a rearrangement of the original expansion yields an expansion in terms of Legendre polynomials. Then, we only need (4.3) to obtain an expansion in terms of spherical harmonics.

The practical realization of this obvious idea was apparently not so easy. As discussed by Steinborn and Filter [15, pp. 269 - 270], many authors had quite a few problems with the determination of explicit expressions for the coefficients of the expansion of Gegenbauer polynomials in terms of Legendre polynomials. Also Steinborn and Filter constructed very messy expressions for these coefficients which are restricted to certain superscripts of the Gegenbauer polynomial [30, Section 3].

However, already at that time a much more convenient expression for these expansion coefficients been available in the mathematical literature. In Exercise 4 on p. 284 of Rainville's book [31], one finds the following expansion of Gegenbauer polynomials in terms of Legendre polynomials, but no explicit proof (compare also [32, Eq. (5.2)]):

$$C_m^\mu(x) = \sum_{s=0}^{\lfloor m/2 \rfloor} \frac{(\mu)_{m-s}\,(\mu-1/2)_s}{(3/2)_{m-s}\,s!} \times (2m-4s+1)\,P_{m-2s}(x)\,. \quad (4.4)$$

Here, $\lfloor m/2 \rfloor$ denotes the integral part of $m/2$.

Expansion (4.4) can be proved via the explicit expression [33, Eq. 7.313.7 on p. 836] for the integral

$\int_{-1}^{1}(1-x)^\alpha(1-z)^{\nu-1/2}C_m^\mu(x)C_n^\nu(x)\mathrm{d}x$. One only has to set $\nu = 1/2$ and perform the limit $\alpha \to 0$, which requires, however, some algebraic trickery.

In this way, the following addition theorem for a reduced Bessel function with half-integral order can be derived [32, Eq. (5.5)]):

$$\hat{k}_{n-1/2}\big(\beta|\boldsymbol{r}_< \pm \boldsymbol{r}_>|\big)$$
$$= \frac{(-1)^n 8\pi}{(2n-1)!!}\,(\beta r_<)^{n-1/2}(\beta r_>)^{n-1/2}$$
$$\times \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}(\mp 1)^\ell\left[Y_\ell^{m^\star}(\boldsymbol{r}_</r_<)\right]^* Y_\ell^m(\boldsymbol{r}_>/r_>)$$
$$\times \sum_{\nu=0}^{n}\frac{(-n)_\nu(1/2-n)_{\ell+\nu}}{\nu!(3/2)_{\ell+\nu}}\,(\ell+2\nu-n+1/2)$$
$$\times I_{\ell+2\nu-n+1/2}(\beta r_<)K_{\ell+2\nu-n+1/2}(\beta r_>)\,. \quad (4.5)$$

Here, we have $|\boldsymbol{r}_<| < |\boldsymbol{r}_>|$. The original version of this addition theorem as derived by Steinborn and Filter [15, Eq. (3.4)] still contains unspecified expansion coefficients of Gegenbauer polynomials in terms of Legendre polynomials.

The addition theorem (4.5) was quite consequential for my later scientific interests. In my diploma thesis [34], which was published in condensed form in [35], I used this addition theorem for the evaluation of simple multicenter integrals of reduced Bessel functions.

5   Convolution Theorems of B Functions

The original topic of Filter's PhD thesis [36] was the construction of addition theorems and their use for the evaluation of multicenter integrals. During these investigations, it became obvious that the use of addition theorems alone would not suffice to permit an efficient and reliable evaluation of the complicated multicenter integrals of exponentially decaying functions. Thus, alternative approaches were necessary.

Starting from the well known addition theorem of the so-called modified Helmholtz harmonics, Filter succeeded in his PhD thesis [36, Sections 7 - 9] to derive with the help of some very skillful mathematical manipulations remarkably compact expressions for convolution, nuclear attraction, and Coulomb integrals of B functions which were later published in [13, 37].

Probably the most spectacular result is the extremely compact expression for the overlap integral

of two B functions with equal scaling parameters $\beta > 0$, which is simply a finite linear combination of B functions [13, Eq. (4.3)]:

$$\int \left[B_{n_1,\ell_1}^{m_1}(\beta, \boldsymbol{r}) \right]^* B_{n_2,\ell_2}^{m_2}(\beta, \boldsymbol{r} - \boldsymbol{R}) \, \mathrm{d}^3 \boldsymbol{r}$$

$$= \frac{4\pi}{\beta^3} \sum_{\ell = \ell_{\min}}^{\ell_{\max}} {}^{(2)} \langle \ell_2 m_2 | \ell_1 m_1 | \ell m_2 - m_1 \rangle$$

$$\times \sum_{t=0}^{\Delta\ell} (-1)^t \binom{\Delta\ell}{t}$$

$$\times B_{n_1+n_2+\ell_1+\ell_2-\ell-t+1,\ell}^{m_2-m_1}(\beta, \boldsymbol{R}). \qquad (5.1)$$

Here, $\langle \ell_2 m_2 | \ell_1 m_1 | \ell m_2 - m_1 \rangle$ is a so-called Gaunt coefficient, which is the integral of three spherical harmonics over the surface of the unit sphere in $\mathbb{R}^3$. A compact review of the properties of Gaunt coefficients plus additional references can be found in [17, Appendix C]. Moreover, it follows from the selection rules satisfied by the Gaunt coefficient (see for example [38, Eq. (3.1)]) that the summation limit $\Delta\ell = (\ell_1 + \ell_2 - \ell)/2$ is a non-negative integer.

For overlap integrals with different scaling parameters $\alpha \neq \beta > 0$, compact finite expressions involving Jacobi polynomials could be derived [13, Eq. (4.6)]. In addition, there are infinite series representations expressing an overlap integral with different scaling parameters as an infinite series of overlap integrals with equal scaling parameters [13, Eq. (4.9)].

Explicit expressions of similar complexity could also be derived for nuclear attraction integrals [13, Eqs. (6.4) and (6.5)] and in particular also for Coulomb integrals, which are six-dimensional integrals and which describe the electrostatic interaction of one-center charge densities represented by B functions [13, Eqs. (7.5), (7.7), (7.10), (7.13), (7.15), and (7.16)]

Since Slater-type functions $\chi_{N,L}^M$ with integral principal quantum numbers $N \in \mathbb{N}$ can be expressed by finite linear combinations of B functions [37, Eq. (6.3)], the remarkably compact formulas for overlap, nuclear attraction, and Coulomb integrals of B functions can be used to write down analogous expressions for the corresponding integrals of Slater-type functions in a straightforward way.

The extremely compact expression (5.1) was the basis for the construction of certain one-range addition theorems by Filter and Steinborn [39]. These addition theorems are expansions in terms of a complete and orthonormal function set based on the generalized Laguerre polynomials. They converge in the

mean with respect to the norm of the Hilbert space $L^2(\mathbb{R}^3)$ of square integrable functions.

For the evaluation of the expansion coefficients of these addition theorems, which are essentially overlap integrals, Filter and Steinborn only had to combine (5.1) with the following expansion of generalized Laguerre polynomials in terms of reduced Bessel functions [18, Eq. (3.3-35)] (see also [39, Eq. (3.17) and Ref. [23] on p. 2736]):

$$\mathrm{e}^{-z} L_n^{(\alpha)}(2z) \;=\; (2n + \alpha + 1)$$

$$\times \sum_{\nu=0}^n \frac{(-2)^\nu \Gamma(n + \alpha + \nu + 1)}{\nu!(n-\nu)!\Gamma(\alpha + 2\nu + 2)} \, \hat{k}_{\nu+1/2}(z). \quad (5.2)$$

6 The Fourier Transform of B Functions

The remarkably compact explicit expressions for overlap, nuclear attraction, and Coulomb integrals published in [13, 37] undeniably constituted a major achievement which provided considerable evidence that B functions indeed play a special role in the theory of multicenter integrals of exponentially decaying functions.

But many open questions remained. Filter had to develop in his PhD thesis [36, Sections 7 - 9] some very sophisticated, but also very complicated mathematical techniques in order to obtain the remarkably simple expressions for the integrals mentioned above. It was by no means clear whether and how these techniques could also be used profitably in the case of more complicated multicenter integrals.

There was also the problem that in the Steinborn group the Fourier transform method, which already at that time had been considered to be one of the most or even the most important techniques for the evaluation of multicenter integrals, had for a long time a very bad reputation and was wrongly believed to be not very useful. This unjustified prejudice was, however, shattered when I showed that B functions possess a Fourier transform of exceptional simplicity:

$$\bar{B}_{n,\ell}^m(\alpha, \boldsymbol{p}) \;=\; (2\pi)^{-3/2} \int \mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} \, B_{n,\ell}^m(\alpha, \boldsymbol{r}) \, \mathrm{d}^3 \boldsymbol{r}$$

$$= (2/\pi)^{1/2} \frac{\alpha^{2n+\ell-1}}{[\alpha^2 + p^2]^{n+\ell+1}} \, \mathcal{Y}_\ell^m(-\mathrm{i}\boldsymbol{p}). \quad (6.1)$$

This is the most consequential and also the most often cited result of my PhD thesis [18, Eq. (7.1-6) on p. 160]. Later, (6.1) was published in [40, Eq. (3.7)]. Independently and almost simultaneously, (6.1) was also derived by Niukkanen [41, Eqs. (57) - (58)].

The exceptionally simple Fourier transform (6.1) gives B functions a unique position among exponentially decaying functions. It explains why other exponentially decaying functions like Slater-type functions with integral principal quantum numbers, bound state hydrogen eigenfunctions, and other functions based on generalized Laguerre polynomials can all be expressed in terms of finite linear combinations of B functions (details and further references can be found in [42, Section IV] or [29, Section 4]).

As remarked above, the derivation of the remarkably compact explicit expressions for overlap, nuclear attraction, and Coulomb integrals of B functions published in [13, 37] was fairly complicated and required considerable mathematical skills. If however, the Fourier transform (6.1) is used, then the derivation of these expressions is almost trivial [43].

The Fourier transform (6.1) of B functions is also a convenient starting point for the evaluation of more complicated multicenter integrals of B functions by a combination of the Fourier transform method with numerical quadratures. This was first done in articles by Trivedi and Steinborn [44], Grotendorst and Steinborn [45, 46], Homeier and Steinborn [47, 48, 49], and Steinborn and Homeier [50], and in the PhD theses of Grotendorst [51] and Homeier [52].

The key problem of this approach is that evaluation by numerical quadrature can become prohibitively difficult because of the highly oscillatory nature of the integrands. In recent years, Safouhi and coworkers greatly enhanced the efficiency of this approach by combining quadrature rules with suitable convergence acceleration techniques (see for example [53, 54, 55, 56] and references therein). This may well be the currently most promising approach for the evaluation of complicated molecular multicenter integrals of exponentially decaying functions.

7   Bessel Potential Spaces

On the basis of our current level of understanding, we can safely claim that the exceptionally simple Fourier transform (6.1) is the most important property of B functions. It fully explains the advantageous features of B functions in the context of multicenter integrals of exponentially decaying functions. Nevertheless, it is certainly legitimate to wonder why it took such a long time to discover both B functions and their Fourier transform (6.1).

For example, Geller [57, 58, 59] had studied in his work on multicenter integrals of Slater-type functions certain types of radial integrals, which contain the radial parts of Fourier integral representations of B functions as special cases. In my opinion, it is hard to understand that neither Geller nor anybody else realized that these special cases deserve special attention because they represent functions with highly useful features.

I found out later that the Fourier transform (6.1) of B functions had at least partly been known before in a completely different context. Aronszajn and Smith [60] showed already in 1961 in connection with their work on functional analytic properties of solutions of certain inhomogeneous partial differential equations that $[1 + |\boldsymbol{\xi}|^2]^{-\alpha/2}$ with $\boldsymbol{\xi} \in \mathbb{R}^n$ and $\alpha > 0$ is the n-dimensional Fourier transform of what we now call a reduced Bessel function with argument $|\boldsymbol{x}|$ with $\boldsymbol{x} \in \mathbb{R}^n$.

Their starting point was the following n-dimensional generalized modified Helmholtz equation:

$$\left[1 - \nabla^2\right]^{\alpha/2} u(\boldsymbol{x}) = g(\boldsymbol{x}). \qquad (7.1)$$

Here, u, $g \colon \mathbb{R}^n \to \mathbb{C}$ are functions, $\boldsymbol{x} \in \mathbb{R}^n$, $\alpha > 0$, and ∇^2 is the n-dimensional Laplacian.

Let us assume that u and g permit n-dimensional Fourier transformation. Then,

$$\bar{u}(\boldsymbol{\xi}) = (2\pi)^{-n/2} \int e^{-i\boldsymbol{\xi}\cdot\boldsymbol{x}} u(\boldsymbol{x})\, d^n\boldsymbol{x}, \qquad (7.2)$$

$$\bar{g}(\boldsymbol{\xi}) = (2\pi)^{-n/2} \int e^{-i\boldsymbol{\xi}\cdot\boldsymbol{x}} g(\boldsymbol{x})\, d^n\boldsymbol{x}, \qquad (7.3)$$

and the Fourier transform of $\left[1 - \nabla^2\right]^{\alpha/2}$ is the function $[1 + |\boldsymbol{\xi}|^2]^{\alpha/2}$. Thus, the partial differential equation (7.1) can be reformulated as follows:

$$\bar{u}(\boldsymbol{\xi}) = \frac{\bar{g}(\boldsymbol{\xi})}{[1 + |\boldsymbol{\xi}|^2]^{\alpha/2}}. \qquad (7.4)$$

Consequently, for a given inhomogeneity $g(\boldsymbol{x})$ the unknown function $u(\boldsymbol{x})$ can be expressed as an inverse Fourier integral:

$$u(\boldsymbol{x}) = (2\pi)^{-n/2} \int e^{i\boldsymbol{x}\cdot\boldsymbol{\xi}} \frac{\bar{g}(\boldsymbol{\xi})}{[1 + |\boldsymbol{\xi}|^2]^{\alpha/2}}\, d^n\boldsymbol{\xi}. \quad (7.5)$$

The inverse Fourier integral on the right-hand side of (7.5) can be expressed as the convolution integral,

$$u(\boldsymbol{x}) = (2\pi)^{-n/2} \int G_\alpha(\boldsymbol{x} - \boldsymbol{y})\, g(\boldsymbol{y})\, d^n\boldsymbol{y}, \quad (7.6)$$

where the so-called Bessel potential $G_\alpha(\boldsymbol{x})$ is defined as follows:

$$G_\alpha(\boldsymbol{x}) = (2\pi)^{-n/2} \int \frac{e^{i\boldsymbol{x}\cdot\boldsymbol{\xi}}}{[1 + |\boldsymbol{\xi}|^2]^{\alpha/2}}\, d^n\boldsymbol{\xi}. \qquad (7.7)$$

Aronszajn and Smith [60, Eq. (2, 10) on p. 414] showed that $G_\alpha(\boldsymbol{x})$ is essentially a reduced Bessel function (compare also Samko's book [61, pp. 184 - 185] and references therein):

$$G_\alpha(\boldsymbol{x}) \; = \; \frac{|\boldsymbol{x}|^{(\alpha-n)/2}\, K_{(n-\alpha)/2}(|\boldsymbol{x}|)}{2^{-1+\alpha/2}\, \Gamma(\alpha/2)} \,. \qquad (7.8)$$

Here, $K_{(n-\alpha)/2}(|\boldsymbol{x}|)$ is a modified Bessel function of the second kind [14, p. 66]

As already discussed in Section 1, it is my conviction that science is now highly fragmented and communication between researchers from different scientific (sub)disciplines does not function particularly well. Bessel potentials provide convincing evidence supporting my claim. For example, mathematicians working with Bessel potentials seem to be completely unaware of the closely related Bessel polynomials and reduced Bessel functions, and in the literature of theoretical chemistry Bessel potentials have apparently been completely ignored so far (an exception is my Habilitation thesis [62, p. 138]).

8 Outlook

Because of their remarkable simplicity in the coordinate representation, Slater-type functions have obvious advantages. However, their molecular multicenter integrals are notoriously difficult.

In contrast, B function have a comparatively complicated structure. Therefore, a more detailed look at their mathematical properties is required to understand why B functions have some highly advantageous features in connection with molecular multicenter integrals. This does not mean that their molecular multicenter integrals are necessarily simple in absolute terms, but they can in most cases be evaluated significantly more easily than the corresponding integrals of Slater-type functions.

Thus, the history of B functions, which is essentially a history of the influx of mathematical knowledge into theoretical chemistry, is well suited to study a question of more profound importance, namely the interaction between mathematics and theoretical chemistry.

I think that I can claim with some justification that the historical development of B functions has not been a straight path, but at best a not completely random walk. Moreover, the available information has not always been utilized effectively, which obviously slowed down progress. Thus, communication problems – not only between mathematicians and theoretical chemists, but also among theoretical chemists – have more or less been the rule rather than the exception.

Since theoretical chemistry is such a highly interdisciplinary field, future progress will depend very much on our ability of minimizing the detrimental effects of a breakdown of interdisciplinary and/or intradisciplinary communication. The history of B functions shows that this may not be so easy.

The topics discussed in this article indicate that progress in theoretical chemistry depends very much on the influx of previously unknown mathematical ideas into theoretical chemistry. It would, however, be wrong to assume that communication between mathematics and theoretical chemistry would necessarily be a one way street. Problems from theoretical chemistry in general and from the theory of B functions in particular can provide valuable inspiration for mathematical research. My own research provides ample evidence that this is indeed possible.

During the work for my PhD thesis [18], series expansions for multicenter integrals played a major role. Since it (too) often happened that my series expansions converged slowly (see for example [16, Table II]), it was a natural idea to speed up convergence with the help of (nonlinear) sequence transformations. To the best of my knowledge, this was first done in 1967 by Petersson and McKoy [63]. Unfortunately, I knew at that time only linear series transformations as described in the classic, but now outdated book by Knopp [64]. Unfortunately, these linear transformations turned out to be ineffective. I was completely ignorant of the more powerful nonlinear transformations, which often accomplish spectacular improvements of convergence.

My ignorance only changed when I did postdoctoral work at the Department of Applied Mathematics of the University of Waterloo in Waterloo, Ontario, Canada, where I – inspired by Jiří Čížek – applied Padé approximants and continued fractions for the summation of divergent power series. After my return to Regensburg, I tried to apply nonlinear transformations also to slowly convergent series expansions for multicenter integrals. In some cases, remarkable improvements of convergence were observed.

In order to understand better the power as well as the limitations of nonlinear sequence transformations, I also worked on their theoretical properties. As a by-product, I was able to derive several new transformations. The majority of these transformations was published in my long article [65], where also

efficient algorithms for the computation of sequence transformations as well as theoretical error estimates and convergence properties are discussed.

Later, I applied sequence transformations successfully in such diverse fields as the evaluation of molecular multicenter integrals of exponentially decaying functions, the evaluation of special functions and related objects, the summation of strongly divergent quantum mechanical perturbation expansions, the prediction of unknown perturbation series coefficients, and the extrapolation of quantum chemical crystal orbital and cluster electronic structure calculations for oligomers to their infinite chain limits of stereoregular *quasi*-onedimensional organic polymers. More information on my work both on and with sequence transformations and exact references can by found in my recent publications [66, 67, 68, 69].

Thus, it is probably justified to claim that numerical mathematics and scientific computing ultimately profited via cross-fertilization from the convergence problems which I encountered during my PhD thesis and also later.

Something similar can be said about the work of Safouhi. As already mentioned in Section 6, he combines numerical quadrature schemes with sequence transformations for the evaluation of the highly oscillatory integral representations for multicenter integrals. Over the years, Safouhi and his coworkers have worked hard and studied numerous different sequences transformations in order to optimize their computational approach. Initially, Safouhi was only interested in the evaluation of molecular multicenter integrals, but recently he could demonstrate that his techniques work very well also in the case of extremely pathological oscillatory integrals that are predominantly of mathematical interest [56].

Let me summarize. It is my conviction that theoretical chemists interested in methodological questions should *actively* seek the collaboration with mathematicians. Both sides have good chances of profiting from such a collaboration.

A Notation and Terminology

For the set of *positive* and *negative* integers, I write $\mathbb{Z} = \{0, \pm 1, \pm 2, \ldots\}$, for the set of *positive* integers, I write $\mathbb{N} = \{1, 2, 3, \ldots\}$, and for the set of *non-negative* integers, I write $\mathbb{N}_0 = \{0, 1, 2, \ldots\}$. The *real* and *complex* numbers are denoted by $\mathbb{R}$ and $\mathbb{C}$, respectively. The set of *three-dimensional vec-*

tors $\boldsymbol{r} = (x, y, z)$ with real components $x, y, z \in \mathbb{R}$ is denoted by $\mathbb{R}^3$.

For the commonly occurring special functions of mathematical physics I use the notation of Magnus, Oberhettinger, and Soni [14] unless explicitly stated otherwise.

For the functions of angular momentum theory – essentially (surface) spherical harmonics $Y_\ell^m(\theta, \phi)$, regular solid harmonics $\mathcal{Y}_\ell^m(\boldsymbol{r})$, and Gaunt coefficients $\langle \ell_3 m_3 | \ell_2 m_2 | \ell_1 m_1 \rangle$ – I use the same notations and conventions as in [17, Appendices B and C].

Fourier transformation is used in its symmetrical form, i.e., a function $f : \mathbb{R}^3 \to \mathbb{C}$ and its Fourier transform $\bar{f}$ are connected by the integrals

$$\bar{f}(\boldsymbol{p}) = (2\pi)^{-3/2} \int \mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}} f(\boldsymbol{r}) \, \mathrm{d}^3\boldsymbol{r}, \qquad \text{(A.1)}$$

$$f(\boldsymbol{r}) = (2\pi)^{-3/2} \int \mathrm{e}^{\mathrm{i}\boldsymbol{r}\cdot\boldsymbol{p}} \bar{f}(\boldsymbol{p}) \, \mathrm{d}^3\boldsymbol{p}, \qquad \text{(A.2)}$$

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